

Physics of Orientation-induced Crystallization in Isotactic Polypropylene

R.H. Somani, B.S. Hsiao, L. Yang (SUNY, Stony Brook), and R.S. Stein (U. of Massachusetts at Amherst)
Beamline(s): X3A2

Introduction: From step-shear induced crystallization studies in isotactic polypropylene using synchrotron x-ray techniques, the physics of orientation-induced crystallization has been examined. We argue that orientation affects the molten chains both thermodynamically and hydrodynamically. The thermodynamic effect involves entropy reduction of oriented chain segments and favors formation of primary nuclei. The hydrodynamic effect generates a network of primary nuclei through the relaxation time difference in chains and also causes realignment of the nuclei, which leads to growth of different morphology.

Methods and Materials: Synchrotron X-ray measurements were carried using a Linkam CSS-450 high temperature shearing stage at the X3A2 Beamline; a 2D MAR CCD detector was used for the detection of 2D scattering patterns.

Results and Discussion: Figure 1 shows a series of 2D small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) patterns of the iPP melt at 175 °C before and after application of step shear (102 s^{-1} shear rate and 1430% strain). Development of discrete scattering maxima in SAXS along the deformation direction was clearly observed while WAXD patterns showed no sign of crystallization. The appearance of the oriented SAXS profile indicates the formation of lamellar structure perpendicular to the flow direction. These observations bring up the interesting questions regarding the nature of the initial structure induced by flow above the nominal melting point that cannot be answered by our current understanding on the subject of orientation-induced crystallization in polymers. Based on our SAXS and WAXD results and the thermodynamic and hydrodynamic effects of flow, a schematic of several stages during orientation induced crystallization are illustrated in Figure 2. Application of flow immediately produces a network of parallel chain segments (bundles), which can be considered as primary nuclei (Figure 2-(2)), depending upon the relaxation time behavior of the chains. Long chains most likely interconnect the adjacent nuclei; the relaxation of the local orientation of the chains in the vicinity of the primary nuclei can cause realignment of nuclei (Figure 2-(3)). Secondary nucleation from the network of oriented primary nuclei lead to a kebab structure containing well-separated lamellar stacks (Figure 2-(4) and -(5)). This is consistent with the SAXS observation that scattering maximum along the flow direction is seen developing with time.

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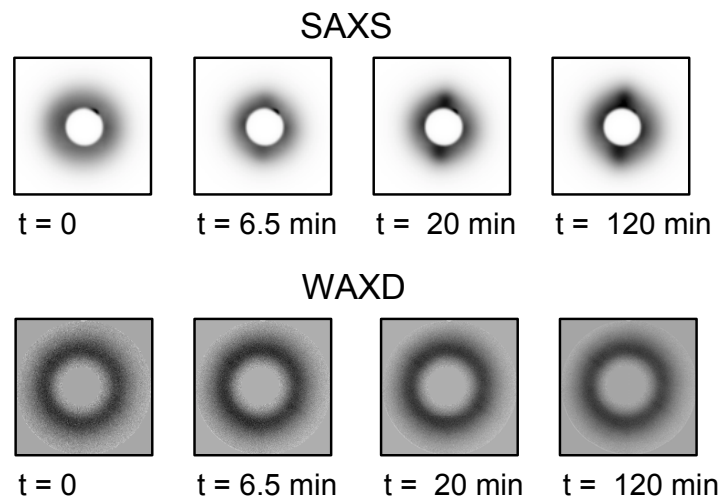


Figure 1: Representative SAXS and WAXD images at selected times after step shear (strain = 1430%, Rate = 102 s^{-1}) at 175 °C.

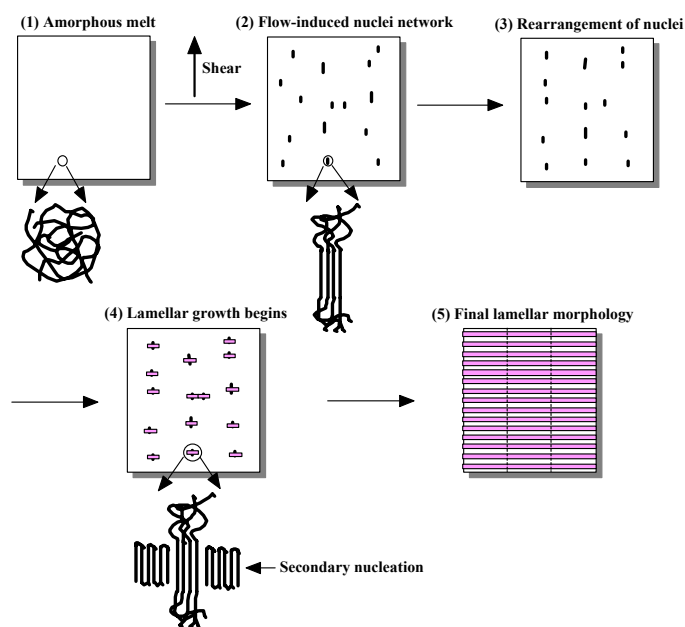


Figure 2: Schematic diagram of flow-induced crystallization - realignment of the nuclei network and subsequent crystal growth.